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CRYSTAL AND MOLECULAR STRUCTURE OF *N*-NITRO-*N*-METHYL-*p*-NITROANILINE: ANALYSIS OF SUBSTITUENT EFFECTS ON THE RING GEOMETRY AND ESTIMATION OF THE HAMMETT SUBSTITUENT CONSTANT FOR THE *N*-METHYLNITRAMINO GROUP

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The crystal and molecular structure of *N*-nitro-*N*-methyl-*p*-nitroaniline was solved with good precision: $R = 0{\cdot}058$ and average estimated standard deviation for bond lengths = 0·003 Å. Analysis of the geometry reveals that the NO_2 attached to the N atom is strongly conjugated. Application of the HOSE model to its geometry and to geometries of 12 other *para*-substituted nitrobenzenes yields good linear regressions between canonical structure weights and Hammett σ values. by interpolation, σ for the $N(Me)NO_2$ group is estimated to 0·36.

INTRODUCTION

The *N*-methylnitramino group is a complex substituent for which substituent parameters such as σ constants[1] or group electronegativity[2,3] are either not well established or not known. Undoubtedly the nitro group substituted at the nitrogen atom of the amino group increases its eletronegativity. In addition, it should be taken into account that the lone pair at the amino group may be involved in cooperative interactions with the π-electron system of the nitro group. These kinds of interactions are usually reflected in the geometry of the molecule or that part of it involved in them.[4]

The aim of this work was to analyse similarities and dissimilarities in the geometry of the title system in comparison with the series of *para*-substituted derivatives of nitrobenzene and a few examples of *para*-substituted derivatives of aniline or its *N*,*N*-dialkyl derivatives.

EXPERIMENTAL

N-Nitro-*N*-methyl-*p*-nitroaniline (NMNA) was synthesized according to the literature procedure[5] by nitration of *N*-methyl-*p*-nitroaniline with fuming nitric acid ($d = 1{\cdot}52$) in acetic anhydride in 83% yield, m.p. 139–140 °C (from EtOH).

A crystal of dimensions $0{\cdot}35 \times 0{\cdot}3 \times 0{\cdot}3$ mm was used for data collection. KM4 KUMA-Diffraction (a Polish diffractometer) was used with graphite monochromated Cu Kα radiation. Unit cell parameters were obtained by a least-squares fit of the setting angles of 25 reflections in θ range $11 \leqslant \theta \leqslant 22°$. The intensities of 1919 reflections were measured, with $\omega - 2\theta$ scans, index range $h \leqslant 10$, $k \leqslant 18$, $-20 \leqslant l \leqslant 20$, $\sin\theta/\lambda \leqslant 0{\cdot}64$ Å^{-1}. The data were corrected for Lorentz and polarization effects but not for absorption. Three reflection (121, 321 and 332) were monitored every 100 reflections. No significant variation was detected (the variation of the intensity control reflections was <5%). Of 1919 measured reflections, 1382 with $F_0 \geqslant 3\sigma(F_0)$ were used in the calculations. The structure was solved by direct methods. Full-matrix least-squares refined minimizing $\Sigma\, w(|F_0| - |F_c|)^2$ with weights $w = [\sigma^2(F_0) + 0{\cdot}00001(F_0)^2]^{-1}$ was employed. Final $R = 0{\cdot}0582$, $wR = 0{\cdot}0617$, $S = 5{\cdot}2235$ for 1382 reflections and 146 parameters. The final difference Fourier map showed $\Delta\rho_{max} = +0{\cdot}21$, $\Delta\rho_{min} = -0{\cdot}23$ e Å^{-3} and average $\Delta/\rho = 0{\cdot}0008$. The computer programs SHELXS-86[6] and SHELX-76[7] were used. The final

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geometrical calculations were performed with the CSU program.[8] The molecular illustrations were drawn using PLUTO.[9] Atomic scattering factors were taken from published tables.[10]

RESULTS AND DISCUSSION

The crystal data for NMNA are given in Table 1, final atomic parameters for heavy atoms are given in Table 2 and the molecular geometry and atom numbering are shown in Figure 1.

$N(Me)NO_2$ is almost perpendicular to the plane of the ring ($\varphi = -72 \cdot 3^\circ$) whereas the other nitro group is almost coplanar with the ring ($\varphi = 2 \cdot 5^\circ$).

Table 1. Crystal data

Molecular formula	$C_7H_7N_3O_4$
Molecular weight	197·15
Space group	*Pcab*
Cell dimensions (Å)	$a = 7 \cdot 249(1)$ $b = 14 \cdot 157(3)$ $c = 16 \cdot 445(5)$
Cell volume (Å³)	$V = 1687 \cdot 7$
Molecular multiplicity	$Z = 4$
Calculated density (g cm⁻³)	1·552
Radiation, λ(Cu Kα) (Å)	1·540562
Linear absorption coefficient (cm⁻¹)	10·73
Reflections $F > 3\sigma(F)$	1382
R	0·0582
wR	0·0617

Table 2. Non-hydrogen fractional atonic coordinates, isotropic/equivalent temperature factors ($A^{**}2$) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
N-1	2372(3)	8396(1)	6239(1)	43(0)
O-1	1958(3)	8791(1)	5607(1)	66(1)
O-2	2708(3)	8819(1)	6869(1)	67(1)
N-2	2991(3)	4442(1)	6256(1)	41(0)
N-3	1519(3)	3864(1)	6226(1)	44(0)
O-3	1823(3)	3013(1)	6232(1)	65(1)
O-4	−31(3)	4230(1)	6202(1)	57(0)
C-1	2446(3)	7357(1)	6251(2)	35(0)
C-2	2990(4)	6914(2)	6957(1)	41(1)
C-3	3113(4)	5935(2)	6958(1)	40(0)
C-4	2693(3)	5441(1)	6261(1)	34(0)
C-5	2112(4)	5893(2)	5561(1)	41(1)
C-6	1993(4)	6871(2)	5552(1)	42(1)
C-7	4819(4)	4036(2)	6316(2)	55(1)

[a] U_{eq} is calculated as[11] (U11*(astar*a)**2 + U22*(bstar*b)**2 + U33*(cstar*c)**2 + 2(U12*astar*bstar*a*b*cos gamma + U13*astar *cstar*a*c*cos beta + U23*bstar*cstar*b*c*cos alpha))/3, where astar, bstar and cstar are reciprocal a, b and c, respectively, and thermal parameters for anisotropic vibrations defined by Cruickshank[12] as $T = \exp(-2^*\text{pi}^{**}2(\text{U11}^*(\text{h}^*\text{astar})^{**}2 + \cdots + 2^*\text{U12}^*\text{h}^*\text{k}^*\text{astar}^*\text{bstar} + \cdots))$.

In order to determine the character of $N(Me)NO_2$ as a substituent, the appropriate bond lengths in NMNA, *p*-dinitrobenzene,[13] *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine[14] and *N*,*N*-diethyl-*p*-nitroaniline[15] are compared in Table 3. Analysis of the differences in the lengths of the appropriate bonds leads to the conclusion that there is a strong similarity between NMNA and *p*-dinitrobenzene: no difference in the appropriate bond length in the ring exceeds 0·4 pm and the difference between the lengths of C_1N_1 is only 0·6 pm. This means that the nitro group interacts with the ring in NMNA almost as strongly as if it was linked directly to the ring. As the dihedral angle between the $N(Me)NO_2$ group and the ring is 72·3°, the interactions seem to be almost entirely a field/inductive effect.

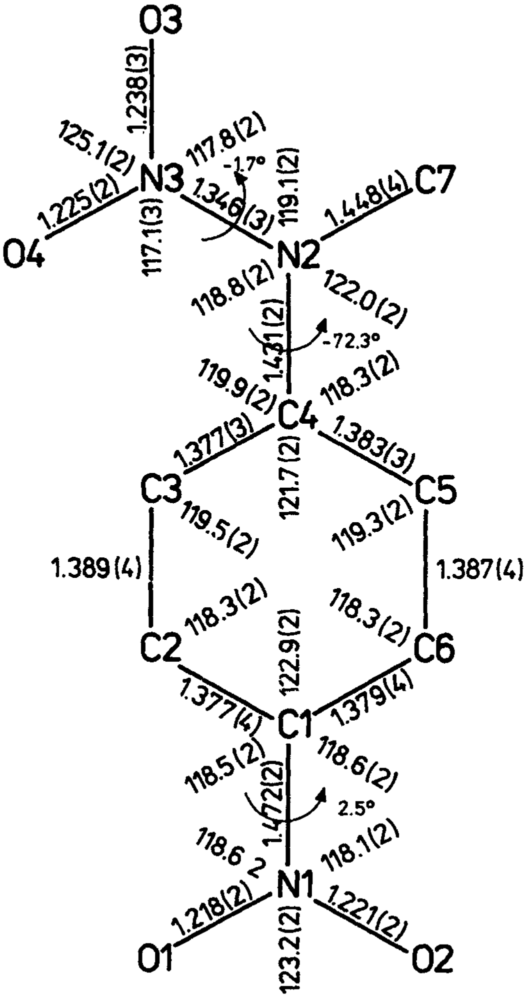
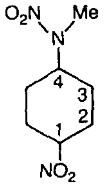
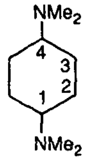
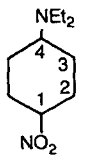


Figure 1. Values of bond lengths, bond angles and dihedral angles between the best ring planes

Table 3. Comparison of bond lengths in NMNA, *p*-dinitrobenzene, *N,N,N′,N′*-tetramethyl-phenylenediamine and *N,N* diethyl-*p*-nitroaniline

Compound	Ref.	Bond length (Å)				
		C_4N	C_4C_3	C_3C_2	C_2C_1	C_1N
	This work	1·431	1·380	1·388	1·378	1·472
	13	1·478	1·376	1·387	1·376	1·478
	14	1·407	1·401	1·390	1·401	1·407
	15	1·433	1·386	1·366	1·420	1·354

Another problem is how the $N(Me)NO_2$ group in NMNA affects the ring bond lengths in comparison with other *p*-nitro-substituted benzene derivatives. It has already been shown[16] that weights of the canonical structures in *p*-nitro-substituted derivatives of benzene follow the Hammett rule well. Here we applied the HOSE model[17] to the geometry of NMNA and 12 *para*-substituted nitrobenzenes, taking into account the canonical structures presented in Figure 2. Values of the canonical structure weights are given in Table 4. Table 5 gives regression and correlation coefficients of the linear dependences

$$\%C(i) = \rho(i)\sigma(X) + \text{constant} \qquad (1)$$

where $\sigma(X)$ represents Hammett substituent constants σ_p for electron-accepting substituents and σ_p^+ for electron-donating substituents (all the σ values used in this analysis were taken from Ref. 1, with the following values for σ: NEt_2 and NMe_2 −1·67, NH_3^+ 0·57, NO_2 0·81, NH_2 −1·47, NHMe −1·57; mean value between σ^+ for NMe_2 and NH_2, COOH 0·44, COO^- −0·05, Ph −0·21, $-O^-$ −2·3, OH −0·91, OMe −0·79); $\rho(i)$ is the slope of equation (1), being a measure of the sensitivity of the weight of the *i*th canonical structure, $C(i)$, on the electron accepting/donating property of the substituent X.

Application of the appropriate canonical structure weights (i = I + II, V and VI) and those calculated for NMNA from experimental bond lengths in equation (1) gives, by interpolation, an average value of $\sigma = 0{\cdot}36$. In view of the above discussion it follows that $\sigma_p(NMeNO_2) = \sigma_{ind}(NMeNO_2)$. Charton[28] gives a value of 0·39 for σ_{ind}, which is in good agreement with our σ_p valve.

Table 4. Canonical structure weights of *p*-nitro derivatives of benzene[a]

					i					
X	I + II		III + IV		V	VI	VII + VIII		IX	Ref.
$N(Me)NO_2$	20	19	11	10	10	5	9	8	8	This work
NMe_2	13	13	14	14	16	9	7	7	8	14
NH_3^+	21	21	9	9	9	5	9	9	9	18
NO_2	21	21	9	9	8	5	9	0·1	9	13
NEt_2(A)	10	11	14	16	17	11	6	6	9	15
NEt_2(B)	12	11	14	14	16	11	7	6	9	—
NH_2	12	12	14	14	16	10	7	7	9	19
NHMe	12	13	13	15	15	10	7	6	8	20
OMe	15	17	10	12	13	7	8	8	10	21
OH(α)	17	17	11	10	11	7	9	9	9	22
OH(β)	17	16	11	10	11	7	9	8	10	23
O^-	9	10	15	15	17	12	6	6	9	24
Ph	13	18	13	12	13	7	7	8	9	25
COO^-(A)	17	18	11	11	11	6	8	9	9	26
COO^-(B)	18	18	11	12	10	5	8	8	8	—
COOH	17	18	12	12	11	6	8	8	8	27

[a] Precision of the weights estimate is ~ 1% or less.

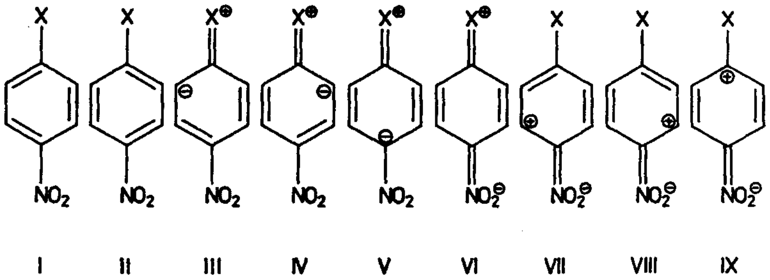


Figure 2. Canonical structures describing *para*-substituted nitrobenzenes

Table 5. Regression and correlation coefficients for equation (1)

i	*ρ*(*i*)	Constant (*i*)	*R*(*i*)
I + II	3·3(3)	17·6(4)	0·891
III + IV	−1·6(2)	11·1(3)	−0·773
V	−2·9(3)	10·9(4)	−0·925
VI	−2·4(2)	6·0(3)	−0·948
VII + VIII	0·83(1)	8·2(2)	0·723
IX	−0·057(19)	8·8(3)	−0·01

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